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Ammonia as a suitable fuel for fuel cells

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Ammonia, an important basic chemical, is produced at a scale of 150 million tons per year. Half of hydrogen produced in chemical industry is used for ammonia production. Ammonia containing 17.5 wt% hydrogen is an ideal carbon-free fuel for fuel cells. Compared to hydrogen, ammonia has many advantages. In this mini-review, the suitability of ammonia as fuel for fuel cells, the development of different types of fuel cells using ammonia as the fuel and the potential applications of ammonia fuel cells are briefly reviewed.

Keywords: fuel cell, ammonia, hydrogen, fuel, storage

INTRODUCTION

Hydrogen is a good energy vector because the only product is water from either combustion or fuel cells. However, on-board hydrogen storage remains a big challenge, which limits the application of hydrogen fuel cells on electric vehicles. Alternatively, hydrogen can be stored in some light chemicals such as ammonia, methanol, ethanol, etc. In terms of CO₂ emission, ammonia is a good indirect hydrogen storage material because it does not contain carbon, therefore, will not release CO₂ when used as fuel in a fuel cell or gas turbine. The energy density of ammonia is 22.5 MJ/kg at HHV, which is about half of that for typical hydrocarbon fuels but higher than metal hydrides (Zamfirescu and Dincer, 2008; Züttel et al., 2010). The raw energy density of liquid ammonia is 11.5 MJ/L, which is higher than the 8.491 MJ/L for liquid hydrogen and the 4.5 MJ/L for compressed H₂ at 690 bar and 15°C¹. Ammonia is a good energy vector for on-board hydrogen storage (Green, 1982; Klerke et al., 2008; Lan et al., 2012). However, safety is regarded as the major drawback of using ammonia as the fuel. Ammonia is toxic but it is detectable by humans in concentrations of just 1 ppm (Reich et al., 2001). Anhydrous ammonia is lighter than air then tends to disperse in the atmosphere. NH₃ would be as safe as the use of gasoline as a transportation fuel (Olson and Holbrook, 2007). The ammonia released from an ammonia tank during a car accident may cause potential safety problem but this can be solved through the application of metal amines with low ammonia partial pressure (Klerke et al., 2008).

Compared to hydrogen, ammonia is easier to be transported. It is much more energy efficient and much lower cost to produce, store, and deliver hydrogen as NH₃ than as compressed and/or cryogenic hydrogen (Figure 1) (Olson and Holbrook, 2007). The infrastructure for ammonia already exists while for hydrogen, new

fueling stations have to be built, which is a big investment (Lan et al., 2012).

Technologies such as fuel cells, combustion engines, and gas turbines using ammonia as the fuel is being developed to recover the energy stored in ammonia (Zamfirescu and Dincer, 2008; Rollinson et al., 2011)^{2,3}. In this mini-review, we focus on the development of direct ammonia fuel cells.

RECENT PROGRESS IN DIRECT AMMONIA FUEL CELLS

ALKALINE AND ALKALINE MEMBRANE DIRECT AMMONIA FUEL CELLS

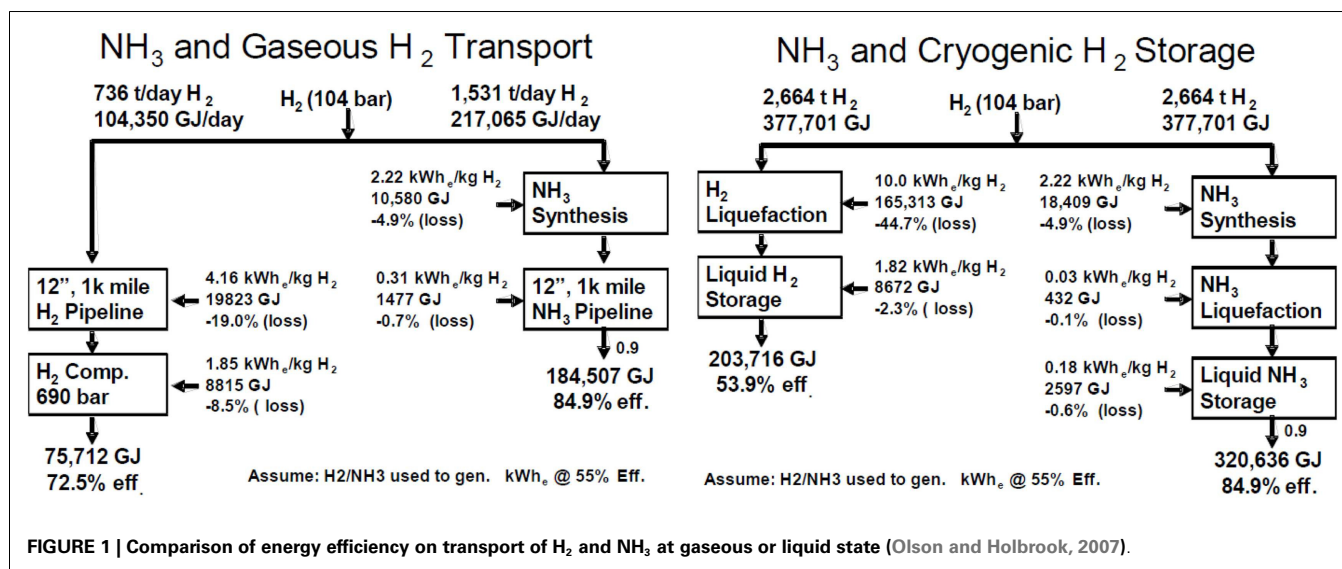
The earliest type of ammonia fuel cells were investigated in 1960s based on alkaline fuel cells (AFCs) using a KOH electrolyte with a typical operating temperature of 50–200°C (Cairns and Simons, 1968). Hejze et al. reported that ammonia can be used for molten hydroxide NaOH/KOH fuel cell at a working temperature of 200–450°C and a power density of 40 mW cm⁻² at 450°C was achieved when nickel was used as both cathode and anode (Ganley, 2008; Hejze et al., 2008). Recently, Yang et al. (2014) investigated the oxidation of ammonia on Pt/C in molten hydroxide electrolyte. It was found that Pt exhibits catalytic activity on ammonia oxidation. However, the durability of ammonia fuel cells operating with KOH-based electrolytes would be a critical issue due to the reaction between hydroxide electrolytes and CO₂ (Lan and Tao, 2010).

Low temperature proton exchange membrane fuel cells (PEMFCs) using hydrogen as the fuel have been developed for various applications including electric vehicles. As for ammonia, it may poison the Pt/C anode catalyst and react with the acidic Nafion membrane. Ammonia itself is not a suitable fuel for PEMFCs. However, ammonia can be used as source for hydrogen production and the produced hydrogen can be fed in PEMFCs for power

¹http://en.wikipedia.org/wiki/Energy_density

²<http://www.spg-corp.com/clean-energy-power-generation.html>

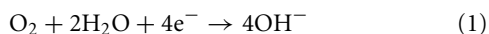
³<http://www.topspeed.com/cars/toyota/2013-toyota-gt86-r-eco-explorer-by-marangoni-tyre-ar149137.html>



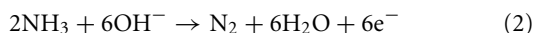
generation (Boggs and Botte, 2009). Besides proton exchange membrane, polymeric alkaline membranes are also developed for fuel cell applications. Ammonia has been tested as fuel for alkaline membrane fuel cells (AMFCs) using nickel anode and MnO₂ cathode (Lan and Tao, 2010).

AMFCs operate under the same principles as traditional AFCs – by the transfer of hydroxide ions through the electrolyte.

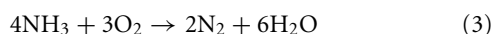
The reaction at the cathode is given by:



and for the anode:



This gives an overall reaction of:



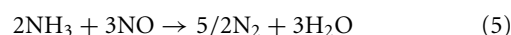
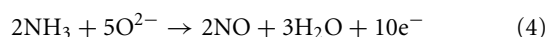
Such ammonia fuel cells have been operated at room temperature but the power density is rather low, which could be related to the low catalytic activity of the electrode materials at low operating temperature (Lan and Tao, 2010). Pt/C, PtRu/C, and Ru/C were investigated as anode for AMFCs and it was found that the order of catalytic activity is PtRu/C > Pt/C > Ru/C (Suzuki et al., 2012).

In AMFCs, although the alkaline membrane can still react with CO₂ to form CO₃²⁻ ions, reducing the OH⁻ ion conductivity but precipitates will not be formed. The problems in conventional AFCs associated to the formation of K₂CO₃ and Na₂CO₃ precipitates due to their reaction with CO₂ in air are avoided.

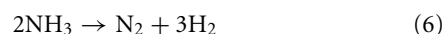
Ammonia fuel cells based on alkaline membrane electrolytes sound attractive but they also have drawbacks: first, it is difficult to identify a good anode and cathode catalysts; second, the cross-over of ammonia through the polymeric membrane electrolyte may decrease the OCV and efficiency (Suzuki et al., 2012); and third, the oxidation of diffused ammonia at cathode may generate toxic NO (Suzuki et al., 2012).

AMMONIA SOLID OXIDE FUEL CELLS

As for direct ammonia fuel cells, up to date the best choice is to operate at high temperature using solid oxide fuel cell (SOFC) technology. Ammonia SOFCs based on both oxygen ion and proton-conducting electrolytes have been reported. Vayenas and Farr reported the first direct ammonia SOFC in 1980 based on yttria stabilized zirconia (YSZ) electrolyte and platinum electrodes for co-generation of electricity and nitric oxide (Vayenas and Farr, 1980; Sigal and Vayenas, 1981). Two electrochemical reactions may happen on the SOFC anode side:



Reaction (4) is rate limiting because of the slow diffusion of O²⁻ through the electrolyte, therefore, NO is produced at the SOFC anode. It was found that, if an iron-based catalyst was used as anode to facilitate the decomposition of ammonia, producing hydrogen and nitrogen according to the following reaction:



then NO is not produced at the anode although an O²⁻ conducting YSZ electrolyte was used (Wojcik et al., 2003; Ma et al., 2007). The thermal decomposition of ammonia itself according to reaction (6) becomes significant at a temperature above 500°C (Perman and Atkinson, 1904). Therefore, it will be beneficiary to run an ammonia fuel cell at high temperature. A high power density of 1.19 W/cm² at 650°C was reported for a direct ammonia SOFC based on oxygen-conducting Ce_{0.8}Sm_{0.2}O_{1.9} electrolyte (Meng et al., 2007). To avoid the formation of nitric oxide, another option is to use a proton-conducting electrolyte based on doped BaCeO₃ and BaZrO₃ (Maffei et al., 2005, 2007; Ni et al., 2008; Zhang and Yang, 2008; Xie et al., 2009). In this case, protons are generated from ammonia or hydrogen decomposed from ammonia then transferred to the cathode to react with oxygen, producing

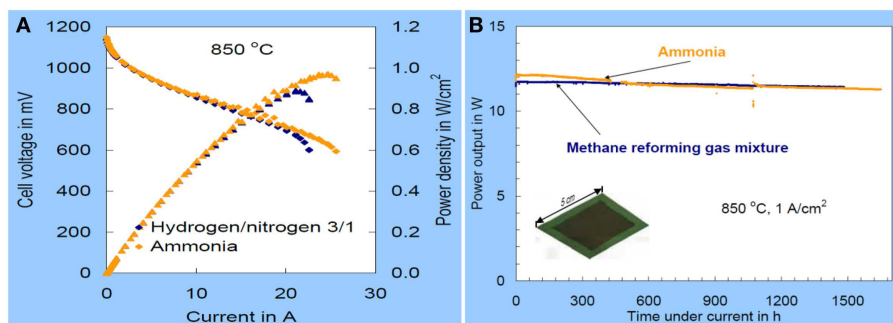


FIGURE 2 | The Current-voltage and power output curves for the use of ammonia or a corresponding hydrogen/nitrogen mixture as fuel at 850°C (A) and power output using ammonia as fuel on a 5 cm × 5 cm SOFC at 850°C, 1 A/cm² current density, ~75–80% fuel utilization (B) (Hagen, 2007).

water. Water is produced at the cathode therefore will not dilute the fuel. Research on ammonia SOFCs has been reviewed by Ni et al. (2009). Ni also carried out modeling of ammonia SOFCs and it was found that increasing the inlet temperature of NH_3 -fueled SOFC is favorable for a higher electric output, but the temperature gradient in the SOFC is considerably higher, particularly near the inlet of the SOFC (Ni, 2011). Thermodynamic analysis indicates that the peak power density of ammonia-fed SOFCs based on proton-conducting electrolytes is 20–30% higher than SOFCs based on O^{2-} ion conducting electrolytes, mainly attributed to the higher concentration of hydrogen at the anode in all cases (Ishak et al., 2012).

As for high temperature ammonia SOFCs, the challenge is the performance durability and costing on fabricating of the cells. It been reported a power density of 1 W/cm² was observed at 850°C with a degradation of 7% over 1500 h when NH_3 was used as fuel in an SOFC (Figure 2) (Hagen, 2007). The degradation was 2% when the simulated mixture of N_2 and H_2 was fueled. The difference could be related to the endothermic ammonia decomposition on the anode. It should be noted that Ni-YSZ cermet anode was used. One of the possible reasons is the formation of NiO or NiN_xO_y at the anode where oxygen partial pressure is quite high at the place close to fuel exhaust (Ningthoujam and Gajbhiye, 2004). The higher degradation could be related to the stability and the microstructure of anode in ammonia. It is believed that the durability of ammonia SOFC could be improved if a redox stable anode is employed in the SOFC stack (Cowin et al., 2011).

CHALLENGES IN DEVELOPING DIRECT AMMONIA FUEL CELLS

The challenges in developing ammonia fuel cells are different for various types of ammonia fuel cells. For low temperature ammonia fuel cells based on polymeric membrane electrolytes, the real challenge is to minimize the cross-over of ammonia and to identify suitable electro-catalysts used as electrodes, particularly the anode (Lan and Tao, 2010). It is difficult to catalytically produce hydrogen from ammonia at low temperature. In other words, it is hard to break the N–H bonds in NH_3 at low temperature. For the anode reaction to be happened at the ammonia AMFCs, it is essential that the N–H bonds in NH_3 have to be split to react with OH^- ions. Based on today's technology, it is difficult to develop a

good low temperature direct ammonia fuel cell with high power density. However, it can be envisaged that direct ammonia fuel cells with good performance would be achievable when the operating temperature increased to 200°C or above.

For ammonia AFCs, unless O_2 or CO_2 -free air is used, the stability of ammonia fuel cells based on hydroxide solution or molten hydroxide electrolytes will be a challenge. Today's polymeric alkaline membrane electrolyte cannot be operated at a temperature above 200°C. However, a good inorganic OH^- ion conductor, which can be used at high temperature, is envisaged to be developed, which will be an ideal electrolyte for ammonia fuel cells. It has been reported Sb (V) and Mo(VI) doped SnP_2O_7 exhibit hydroxide conduction at a temperature around 200°C (Hibino et al., 2012; Hibino and Kobayashi, 2013). It should be noted that it is controversial that the ionic conduction of doped SnP_2O_7 could be related to the residual H_3PO_4 under the circumstance the chemical compatibility between ammonia and these electrolytes would be a problem. Similarly, proton-conducting materials based on acidic properties cannot be used as electrolyte for ammonia fuel cells due to the reaction between ammonia and acids, reducing the proton conductivity (Li et al., 2003). However, a solid proton conductor, which is chemically compatible with ammonia, like doped $\text{BaCeO}_3/\text{BaZrO}_3$ but can be operated at lower temperature will be a potential electrolyte for intermediate temperature ammonia fuel cells. A big advantage of ammonia fuel cells based on inorganic OH^- or H^+ ion conducting electrolytes is that, the cross-over of ammonia will be minimized.

For direct ammonia SOFCs, the key challenge is the integration of robust redox stable anode to the fuel cell to improve the durability of the anode/electrolyte interface, which can sustain the local temperature change during the operation of the ammonia fuel cells and to avoid formation of nitrides. It is expected that this will improve the durability of direct ammonia SOFCs. To completely avoid the formation of NO_x , ammonia SOFCs based on proton-conducting electrolytes will be a better choice.

CONCLUSION

Ammonia, as a mass produced, low cost chemical is an ideal energy vector. Developments of alkaline, alkaline membrane, and SOFCs using ammonia as the fuel have been made in overcoming the barriers to the widespread use of such systems. However,

it is not at a stage for commercialization yet and further investigation is required. Ammonia offers a clean and reliable source of energy, without many of the problems associated with the traditional hydrogen economy. However renewable ammonia production must be increased in order for ammonia fuel cells to be a truly sustainable source of energy. Electrochemical synthesis of ammonia will play an important role in this area (Amar et al., 2011). The combination of ammonia production from renewable resources and ammonia energy recovery technologies will form key parts of ammonia economy (Lan et al., 2012).

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